

Diffusive Movement of Simazine and Lindane in River-Bed Sediments[†]

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Abstract: River-bed sediments are active zones for pesticide deposition and subsequent movement by diffusion, mass transport and sorption to solids. The aim of this work was to investigate the importance of diffusion as a means of pesticide movement. In laboratory experiments, simazine and lindane were introduced to well-mixed aqueous solutions overlying two different river sediments. Sediment cores were sectioned horizontally and analyzed for pesticide content by supercritical fluid extraction. Experiments were used to determine sorption isotherms of the compounds to suspended sediments at 10°C. Vertical profiles of the pesticides in the sediments showed that the compounds reached a maximum depth of 89 mm over a period of 37 days.

A mathematical model was developed to describe pesticide transport by diffusion within the sediment porewaters and sediment sorbed phases, taking into account sorption of the compounds to sediment particles. Effective diffusion coefficients ($(0.5\text{--}1.6) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) were obtained for simazine and lindane in the characterized sediments. These were used to calculate values for diffusion in the dissolved phase (0.38×10^{-10} and $6.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for simazine and lindane respectively) and diffusion in the sorbed phase ($0.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for simazine and negligible for lindane). Sorption onto the sediment significantly influenced the rate of penetration of the compounds into the sediment; thus although lindane had a larger effective diffusion coefficient than simazine, its larger sorption affinity and negligible diffusion in the sorbed phase led to less penetration into the sediment. © 1998 Society of Chemical Industry

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Key words: simazine; lindane; diffusion; sorption; river sediments

NOTATION

α variable in equation (8)
 p porosity coefficient, unitless
 x sediment depth, m
 c concentration of pesticide in porewater, mol m^{-3}
 a_s concentration of pesticide on solid, mol m^{-3}
 S_{cs} cross-sectional area, m^2

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D' effective diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
 D_s diffusion coefficient of dissolved molecules in porewater, $\text{m}^2 \text{ s}^{-1}$
 D_a diffusion coefficient of sorbed molecules, $\text{m}^2 \text{ s}^{-1}$
 t time, s
 Γ Henry's constant, m
 Γ' reduced Henry's constant, unitless
 Σ specific surface area of the sediment, $\text{m}^2 \text{ kg}^{-1}$
 ρ_s particle density, kg m^{-3}
 C concentration of pesticide in overlying solution, mol m^{-3}
 L depth of overlying solution, m
 K_d sorption coefficient, $\text{m}^3 \text{ kg}^{-1}$

n_a amount of pesticide sorbed, mol kg^{-1} (dry sediment)

INTRODUCTION

Previous work on the distribution of hydrophobic organic contaminants in river-bed sediments has concentrated on those at the surface, typically less than 5 cm in depth.¹⁻⁴ The distribution of such contaminants often shows large temporal and spatial variations in the surface sediments and is normally associated with particulate matter and rates of deposition of suspended particles.^{1,3} The aim of the present work was to investigate the extent to which diffusion affects the distribution of organic compounds with depth of river sediment. This study represents the first published work investigating the movement of pesticides with depth in river-bed sediments.

The depth distribution of polyaromatic hydrocarbons, polychlorobiphenyls and organochlorine pesticides has been investigated in lake sediment,^{5,6} estuarine sediment⁷ and sea-bed sediment cores.⁸ Penetration of these compounds and their derivatives has been observed below pre-industrial sediments^{5,6} and below a contaminated sludge layer.⁸ Field work has shown a similar situation exists for river sediments, with penetration of contaminants into Eocene sub-strata underlying a river bed.⁹ This could potentially lead to contamination of ground- and drinking-water supplies, especially in situations where there is good hydraulic conductivity with nearby aquifers.

Possible modes of contaminant transport are: (a) diffusion whereby compounds become soluble in porewater and diffuse down the concentration gradient,^{8,10} (b) mass transport¹¹ by which infiltrating river water may exchange with groundwater, depending on the water gradient between the river and sediments, and on the nature of the hydraulic contacts (through porosity and permeability);¹² (c) movement when attached to dissolved organic carbon, which is particularly important for more hydrophobic compounds and where dissolved organic carbon concentrations are high;^{13,14} (d) movement as colloids when attached to clay particles,¹⁵ and (e) redistribution as a result of physical mixing of sediment by benthic macrofauna.^{16,17}

Diffusion coefficients for organic contaminants in bulk water are typically $5\text{--}10 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.¹⁷ The presence of a solid decreases the diffusion coefficient because of sorption and sediment geometric effects, where the particle size, particle packing, pore diameter and porosity act to differing degrees in causing the compound to deviate from its original straight-line path in bulk water.¹⁰ Thus the effective diffusion coefficient of an organic pollutant in a saturated sediment is dependent on diffusion in the dissolved and sorbed phases,

the sorption affinity to surfaces and the sediment's geometric characteristics.

This paper describes investigations of the sorption and molecular diffusion of simazine and lindane in a settled river sediment. Other modes of transport were minimized by ensuring no vertical water infiltration, low concentrations of dissolved organic carbon and clay, and the absence of macro invertebrates greater than 2 mm in size. Pesticides were introduced to a slowly stirred, aerated aqueous solution of potassium hydrogen carbonate of similar ionic strength and pH to riverwater, overlying a stationary sediment at 10°C. Changes in pesticide concentration in the aqueous phase and pesticide penetration rate in sediment cores were measured. These were interpreted using a model to describe changes in pesticide concentration in solution and in the development of a sediment profile of the pesticides.

2 THEORY

In sediments there exist both a solid phase (the sediment particles) and pore space (the space between the sediment particles and voids in the particle structure) so that

porosity coefficient,

$$p = \frac{(\text{bulk volume} - \text{solid volume})}{\text{bulk volume}} \quad (1)$$

For a plug of sediment, depth Δx , cross-sectional area S_{cs} :

$$\text{solid volume} = \Delta x S_{cs} (1 - p) \quad (2)$$

In the experiments described below, an aqueous solution overlies a saturated sediment initially containing no pesticides. At the start of the experiment, pesticides were introduced to the overlying solution. The sorption kinetics may be described by a one-dimensional, semi-infinite diffusion model with adsorbate binding. If there are no losses of pesticide through degradation or other processes, then a mass balance is expected between the increase in the amount of pesticide in the sediment and the decrease in the amount of pesticide in the overlying solution, i.e.

$$S_{cs} \rho_s (1 - p) \int_0^\infty n_a(x, t) dx = [C(0) - C(t)] L S_{cs} \quad (3)$$

where S_{cs} is the cross-sectional area, ρ_s is the particle density, p is the porosity coefficient, n_a is the amount of pesticide sorbed (for dry sediment), x is the depth of sediment, t is the time, C is the concentration of pesticide in the overlying solution and L is the depth of

overlying solution.

The concentration change in the sediment can be related to the diffusion of both dissolved and sorbed molecules so that

$$p \frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2} \quad (4)$$

where D_s is the diffusion coefficient of dissolved molecules and c is the concentration of pesticide in porewater. Similarly for sorbed molecules,

$$(1 - p) \frac{\partial a_s}{\partial t} = D_a \frac{\partial^2 a_s}{\partial x^2} \quad (5)$$

where a_s is the concentration of pesticide on the solid and D_a is the diffusion coefficient of sorbed molecules.

Sorption at low adsorbate concentrations is given by the Henry's Law isotherm:

$$a_s = \Gamma c \rho_s \Sigma \quad (6)$$

where Γ is the Henry's constant and Σ is the specific surface area of the sediment. Substituting the adsorbate concentration from (6) into (5), then adding to (4) leads to:

$$\frac{\partial c}{\partial t} = \alpha^2 \frac{\partial^2 c}{\partial x^2} \quad (7)$$

where

$$\alpha^2 = \frac{D_s + D_a \Gamma \rho_s \Sigma}{p + \Gamma \rho_s \Sigma (1 - p)} \quad (8)$$

An effective diffusion coefficient in the sediment, D' may be defined in terms of two components, D_s and D_a . D_s is the diffusion coefficient for dissolved molecules in the porewater and D_a is the diffusion coefficient of molecules in the surface layer. Thus,

$$D' = D_s + \Gamma' D_a \quad (9)$$

where the reduced Henry constant,

$$\Gamma' = \rho_s \Sigma \Gamma \quad (10)$$

Substituting (9) and (10) into (8),

$$\alpha^2 = \frac{D'}{p + \Gamma'(1 - p)} \quad (11)$$

By reducing parameters:

$$\tau = \frac{t\alpha^2}{L^2} \quad \xi = \frac{x}{L}$$

and substituting into (7) leads to

$$\frac{\partial c}{\partial \tau} \frac{\alpha^2}{L^2} = \alpha^2 \frac{1}{L^2} \frac{\partial^2 c}{\partial \xi^2} \quad (12)$$

so that:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial \xi^2} \quad (13)$$

The differential equation (7) is solved for $c(x, t)$ using the Laplace transform, with conditions $c(0, t) = C(t)$ and $c(x, 0) = 0$. Thus the concentration in the sediment is:

$$c(x, t) = (p + \Gamma'(1 - p)) \frac{1}{2\alpha\sqrt{\pi}} \int_0^t \frac{x}{\tau^{3/2}} \times \exp\left(\frac{-x^2}{4\alpha^2\tau}\right) C(t - \tau) d\tau \quad (14)$$

and concentration in solution:

$$C(t) = \frac{2}{\sqrt{\pi}} \exp(\pi A^2 t) \int_{A(\pi)^{1/2}}^{\infty} \exp(-\xi^2) d\xi \quad (15)$$

where

$$A = \sqrt{\frac{D'(p + \Gamma'(1 - p))}{\pi L^2}}$$

and α has been defined in eq. (11).

Equations (14) and (15) predict the movement of pesticides in a homogeneous sediment as a result of molecular diffusion and sorption. Given information about the solution depth and sediment porosity, transport is predicted as a function of both the effective diffusion coefficient (D') and the sorption affinity of the compound as characterized by the distribution coefficient K_d (where $K_d = \Gamma/\rho_s$ and is measured by separate sorption experiments).

A program has been written in MathCad to calculate both $C(t)$ and $c(x, t)$ for chosen values of K_d , solution depth (L) and sediment porosity (ρ_s). The effective diffusion coefficient (D') is calculated using the Minerr function¹⁸ to find the minimum in the residual (Res);

$$Res(D') = \sum_{x, t} \{c^{obsd}(x, t) - c^{calcd}(x, t, D')\}^2 + \sum_t \{C^{obsd}(t) - C^{calcd}(t, D')\}^2 \quad (16)$$

TABLE 1
Characteristics of Sediments I and II.

| Characteristic | Sediment I | Sediment II |
|--|---------------|---------------|
| Particle size distribution | | |
| Clay % <2 µm | 0.4 | 0.7 |
| Silt % 2–63 µm | 4.6 | 9.02 |
| Sand % 63–850 µm | 95.1 | 90.3 |
| Total Organic Carbon (%); | 0.33 (0.08) | 0.86 (0.40) |
| Dry bulk density (g cm ⁻³) | 1.24 (0.04) | 1.27 (0.05) |
| Particle density (g cm ⁻³) | 2.67 (0.05) | 2.67 (0.05) |
| Porosity (%) | 53.6 (1.4) | 52.5 (1.8) |
| Surface area (m ² g ⁻¹) | | |
| [+ c-value] | 1.1 [118] | 1.4 [112] |
| CEC (cmol _c kg ⁻¹) | 2.9 (0.5) | 6.9 (0.8) |
| Fe ₂ O ₃ (%) | 0.027 (0.003) | 0.050 (0.006) |

Standard deviations in parens except for specific surface area where the c-value for the BET method is given.

where c^{obsd} and c^{calcd} are the observed and calculated pesticide concentrations in the sediment, and C^{obsd} and C^{calcd} are the observed and calculated pesticide concentrations in the overlying solution. According to eqns (11)–(15), the calculated quantities depend on D' as a parameter.

3 EXPERIMENTAL METHODS

3.1 Materials used

Simazine and lindane¹⁹ were purchased from Promochem Ltd, Hertfordshire. Potassium hydrogen carbonate (AR grade) was purchased from BDH, Poole. This was used as the background electrolyte to give a similar ionic strength and pH to those of hard waters. A stock

solution of simazine and lindane (200 mg litre⁻¹) was prepared in ethyl acetate and 15 ml was added to a 1-litre flask and the ethyl acetate evaporated under nitrogen. One litre of 10 mM KHCO₃ was added and the solution stirred overnight with a magnetic follower. The solution was filtered through a 0.45-µm, 47-mm diameter, cellulose nitrate filter and stored at 4°C. This produced a stock pesticide solution of ~3 mg litre⁻¹ of similar ionic strength and pH to hard-water rivers.

Two sediments were used. Sediment I was a typical river-bed sediment, a sandy loam from the River Frome which is a chalk stream near the IFE, River Laboratory in East Stoke, Dorset (NGR SY868869). It was collected on 22 April 1996 using a stainless steel scoop to a sediment depth of 10 cm and sieved to <2 mm. Sediment II was artificially prepared to increase the organic carbon content and specific surface area. It consisted of well-mixed River Frome sediment with the addition of 10% w/w Millstream Pond sediment, the latter being an organic-rich silt loam from a nearby pond (NGR SY869868). This pond is fed from river water from the Frome and accumulates organic-rich fine material throughout the year. Collections for Sediment II were on 8 January 1997; the River Frome sediment was sampled as previously described and the Millstream Pond sediment was collected using a fine mesh net to a depth of 10 cm and then sieved likewise.

3.2 Sediment characterization

Mineralogy was determined by X-ray diffraction using a Philips PW1710 diffractometer. The particle sizes were characterised using a Coulter analyser after dispersing the sample in 1% Calgon. Dry bulk density,²¹ particle density²² and porosity²³ were determined, as were cation exchange capacity (CEC),²⁴ and total organic carbon (TOC) by wet titration.²⁵ The iron oxide content was determined by extraction with sodium dithionite and analysis of the extract on a colorimeter. Surface area was determined on a Coulter SA 3100 instrument outgassing the sample (~3 g) at 60°C for 12

TABLE 2

Adsorption Coefficients at 10 (±0.5)°C with Corresponding Pearson's Correlation Coefficient (R^2), Henry's Constant ($\Gamma = K_d/\Sigma$) and K_{oc} for pesticide/sediment systems

| Compound | Sediment I | | | | Sediment II | | | |
|------------|------------------------------------|-------|------------------------------------|---------------------------------------|------------------------------------|-------|------------------------------------|---------------------------------------|
| | K_d (litre kg ⁻¹) | R^2 | Γ (× 10 ⁻⁶ m) | K_{oc} (litre kg ⁻¹) | K_d (litre kg ⁻¹) | R^2 | Γ (× 10 ⁻⁶ m) | K_{oc} (litre kg ⁻¹) |
| Simazine | 0.13 | 0.16 | 0.12 | 10 | 0.41 | 0.75 | 0.30 | 48 |
| Lindane | 3.65 | 0.80 | 3.31 | 1106 | 4.08 | 0.99 | 2.91 | 474 |
| Average pH | 7.8 | | | | 7.5 | | | |

Seven sorption points were determined for an isotherm.

TABLE 3
Sorption Coefficients for Simazine and Lindane selected from the Literature

| <i>Sediment type</i> | K_d (litre kg ⁻¹) | K_{oc} (litre kg ⁻¹) | K_{om} (litre kg ⁻¹) | <i>Reference</i> |
|----------------------------------|------------------------------------|---------------------------------------|---------------------------------------|------------------|
| <i>Simazine</i> | | | | |
| | | 32 | | 31 |
| Fine sand | 0.59 | 63 | | 32 |
| Sand | 0.8 | 131 | | |
| Fine sand | 0.29 | 58 | | |
| Fine sand | 0.73 | 119 | | |
| Fine sand | 0.55 | 45 | | |
| Fine sandy loam | 1.06 | 76 | | |
| Fine sand | 0.85 | 51 | | |
| | 2.9 | | 193 | 33 |
| Unstated | 5.4 | | 234 | |
| | 1.9 | | 142 | |
| | 0.9 | | 112 | |
| | 5.6 | | 125 | |
| | | 500 | | 34 |
| Unstated | | 204 | | 20 |
| Lias clay | 4.03 | 128 | | 35 |
| Bed sediment | 6.84 | 7000 | | |
| Bed sediment | 6.111 | 171 | | |
| Bed sediment | 30.3 | 702 | | |
| Average for mineral soils | 1.9 | | | 36 |
| <i>Lindane</i> | | | | |
| River sediment | | | 316–2512 | 2 |
| Unstated | | 1300 | | 37 |
| | | 2000 | | 20 |
| Montmorillonite | 1.3 | | | 38 |
| Suspended solids/estuarine water | | 2400–4790 | | 39 |
| Peat humic acid | | 730 | | 40 |
| Soil humic acid | | 140 | | |
| Average for mineral soils | 25 | | | 36 |

h. The sorption results were analysed using the BET equation.²⁶

3.3 Organic analyses

Water samples (20 ml) were extracted using solid-phase extraction C₁₈ adsorbent columns (ISOLUTE, 6 ml) and eluted with ~2 ml ethyl acetate. Sediment samples (c.10 g, dry weight) were extracted by supercritical fluid extraction (SFE) with a Dionex system (SFE-703), using SFC/SFE grade carbon dioxide a Co-Solvent Addition Module, with 10% pesticide grade methanol, and a Jun-Air 18-50 compressor. The extract of 1 ml was then spiked with 10 µl of an internal standard of 0.46mg litre⁻¹ ametryn. Detection was by GC/MS with split/splitless injection using a fused-silica capillary column (25 m, 0.2 mm ID, 0.33 µm film thickness, 5% phenyl-methylpolysiloxane stationary phase). Analysis was by Select Ion Mode (SIM), quantifying using the base ions (*m/z* 201 and 181 for simazine and lindane respectively)

with confirmation by a qualifier ion (*m/z* 186 and 219 for simazine and lindane respectively).

Recoveries for solid-phase extraction were 116 ± 8% simazine and 88 ± 18% lindane. Recoveries for SFE were 65% simazine and 54% lindane.²⁷ Trifluralin was also used in the experiments but has not been reported because of very variable recoveries and a poor mass balance, caused by strong sorption to container surfaces, photolysis²⁸ and volatilisation.²⁹

3.4 Isotherm measurements

Sorption isotherms were determined for the pesticides on suspended solids of Sediments I and II in a series of batch experiments with seven determinations per isotherm. The sorption isotherms for the compounds in both sediments were determined over concentration ranges of 0.01–0.41 µg ml⁻¹ for simazine and 0.01–0.64 µg ml⁻¹ for lindane. Each sediment (50 g, dry weight) was suspended in KHCO₃ (10 mM; 200 ml) at

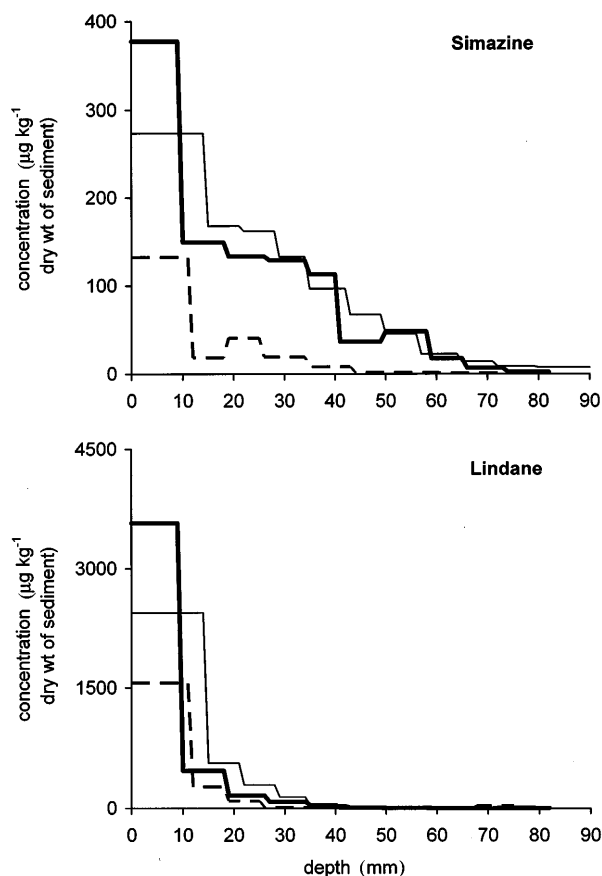


Fig. 1. Pesticide concentration profiles in Sediment I at sample times of (---) seven days, (—) 19 days, and (—) 37 days.

$10(\pm 0.5)^{\circ}\text{C}$ overnight and known amounts of pesticide were then added. Two blanks were also included. Each experiment lasted 24 h before the suspension was centrifuged at $6000\text{ g}_{\text{av}}$ for 15 min. The concentration of pesticide in the overlying solution was measured by solid-phase-extraction as described above, followed by analysis by GC/MS.

3.5 Concentration profile measurements

The uptake of the pesticides from solution and development of concentration profiles in the underlying sediments were measured in two experiments with sediments I and II contained in Pyrex pots in a water bath controlled at $10(\pm 0.5)^{\circ}\text{C}$. All glass equipment was cleaned by soaking in surfactant solution overnight and washing three times in distilled water. After drying, the equipment was rinsed three times in acetone and then ethyl acetate. Three 2-litre pots, with lids, were placed in a water bath maintained at $10(\pm 0.5)^{\circ}\text{C}$. In experiment I, sediment I was added to a depth of 8 cm and 10 mM KHCO_3 added carefully, with little disturbance of the sediment, to a final total volume of 1400 ml. The pots were left in a water bath overnight and then 500 ml of

stock pesticide solution (Section 3.1) was carefully added. The solution was stirred at 24 min^{-1} (with no disturbance of the sediment), and aerated through a glass frit. In experiment I, two further pots were included to assess the degradation of the pesticides at weekly intervals through the course of the experiment in the absence of sediment, and also to check for contamination of the overlying water by the sediment after 14 days. Experiment II was a repeat of experiment I but using sediment II in the pots.

After a requisite period (seven, 19 and 37 days for experiment I and seven, 14 and 28 days for experiment II), five 20-ml samples were taken from the bulk solution and then the remaining solution siphoned off. An inverted 250-ml beaker was forced vertically into the sediment. The 2-litre pot was then inverted and the beaker removed, containing a sediment core. This core was inverted onto a solvent-washed stainless-steel tray, and cut into $\sim 8\text{-mm}$ horizontal sections. Each sediment section was placed into a solvent-washed foil container, frozen and freeze dried. Mixed sediment samples ($c.10\text{ g}$ dry weight) from the foil containers were taken in duplicate.

4 RESULTS AND DISCUSSION

Sediment characterisation showed that both sediments were composed mainly of quartz and calcite. They had similar values for porosity, dry bulk density and particle density (Table 1). However, sediment II had more organic carbon, and silt (Table 1), resulting in a greater cation exchange capacity and surface area. The BET 'c-value', a measure of the strength of nitrogen adsorption to the surface,²⁶ was similar for both sediments indicating a similar strength for surface interactions. The sediment characterisations for River Frome and Millstream Pond sediments are similar to those obtained at these sites by Thirkette & Barrett (1994).³⁰

The sorption isotherms were linear and produced distribution coefficients shown in Table 2. Simazine in Sediment I had a low correlation coefficient (0.16), owing to very variable results at low concentrations. The distribution coefficients are comparable with those found in the literature (Table 3) but tend to be lower because of the low organic carbon and clay contents of these sediments. The sorption coefficients (K_d) were normalised with respect to surface area and organic carbon, producing the Henry's constants (Γ) and K_{oc} values respectively (Table 2). Simazine had a very low K_d in Sediment I, which increased 3-fold in Sediment II. The ratio of the Henry's constants for simazine for Sediments I: II (0.4) is greater than the ratio of the K_d values (0.3). However, the ratio of the K_{oc} of Sediment I: Sediment II is less (0.2). This indicates that the increase in K_d for simazine from Sediment I to II is influenced

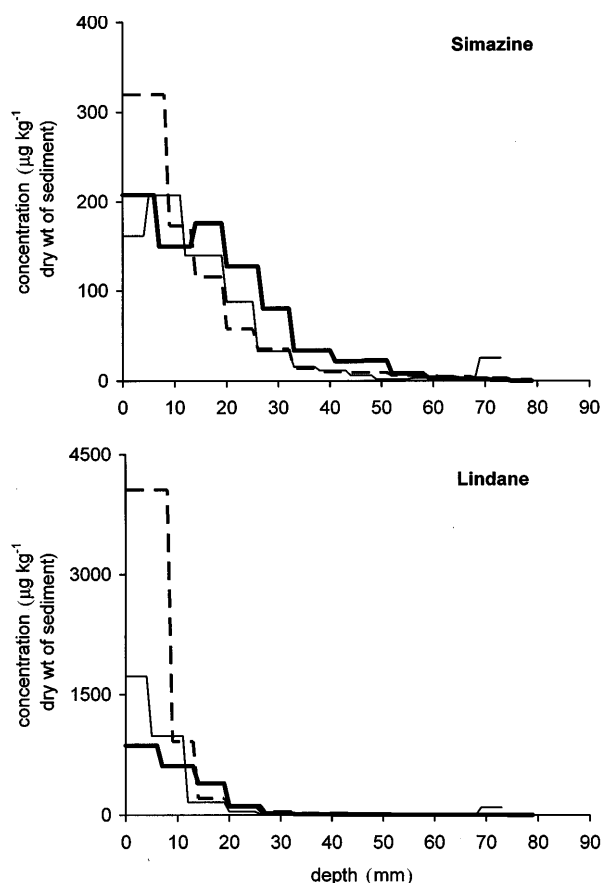


Fig. 2. Pesticide concentration profiles in Sediment II at sample times of (---) seven days, (—) 14 days, and (—) 28 days.

more by the increase in surface area than organic carbon content. The K_d values for lindane in both sediments are similar, as are the Henry's constants. However, normalising with respect to organic carbon reverses the order of lindane sorption between the sediments, with K_{oc} for lindane in Sediment I being over twice as large as the value in Sediment II. Normalising with respect to cation exchange capacity also reverses the order of lindane sorption. It is only when the K_d values are normalized with respect to iron oxide content that the initial order of lindane sorption is maintained. Hence it is possible that it is the increase in iron oxide content which increases lindane's sorption on these sediments, and that surface area has little effect and organic carbon an adverse effect. Iron oxide content does not affect simazine in this way. The adverse effect of organic carbon on the sorption of both compounds suggests that it could be existing as discrete particles, blocking the sites available for sorption on mineral surfaces. It should be noted that the composition of the organic matter in the two sediments could be different, so making void the comparison of K_{oc} values between the sediments.

The results for the sediment concentration profiles and changes in pesticide concentration in the overlying

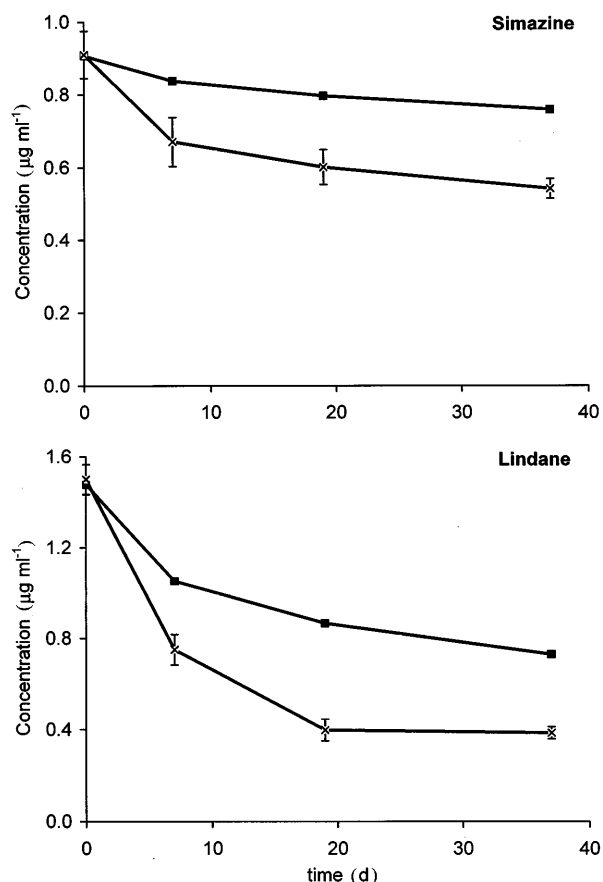


Fig. 3. Comparison of (... × ...) observed and (—■—) loss of simazine from the overlying solution above Sediment I with error bars of the standard deviation for the experimental results.

solution are shown in Figs 1, 2, and 3. Monitoring of pesticide concentrations in aqueous solution with no sediment showed there was no simazine loss during the experiment. However, there was some loss of lindane by Day 45, possibly through volatilisation.⁴¹ Mass balances (eqn (1)) are shown in Figures 4 and 5. Student's *t*-tests showed the mass balances for simazine to be in reasonable agreement except for Sediment II on Day 7. The mass balance for lindane in Sediment I is good but in Sediment II the agreement is only good for Day 7; thereafter there is a noticeable decrease in the amount of lindane recovered from the sediment. This may be a result of lindane becoming more difficult to extract from the sediment with time. Similar results have been observed by Camel *et al.*⁴², where ageing of the sample influenced the percentage of contaminant recovered, depending on the sediment type and contaminant.

The concentration profiles show simazine and lindane concentrations decreasing with sediment depth, with greater depths being reached with time (Figs 1 and 2). In each sediment, lindane concentrations are ten-fold greater than those of simazine, whereas lindane penetrates the sediments less deeply (Figs 1 and 2). Pesticide concentrations increased with time in the top layer

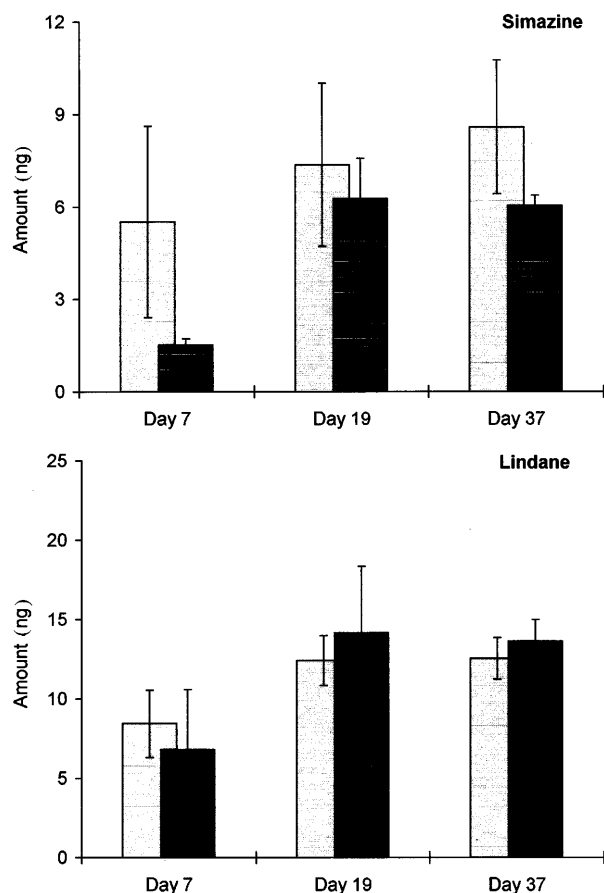


Fig. 4. Mass balance for Sediment I comparing (□) losses of the compounds from the overlying solution with (■) gains in the sediment; error bars show the standard deviation.

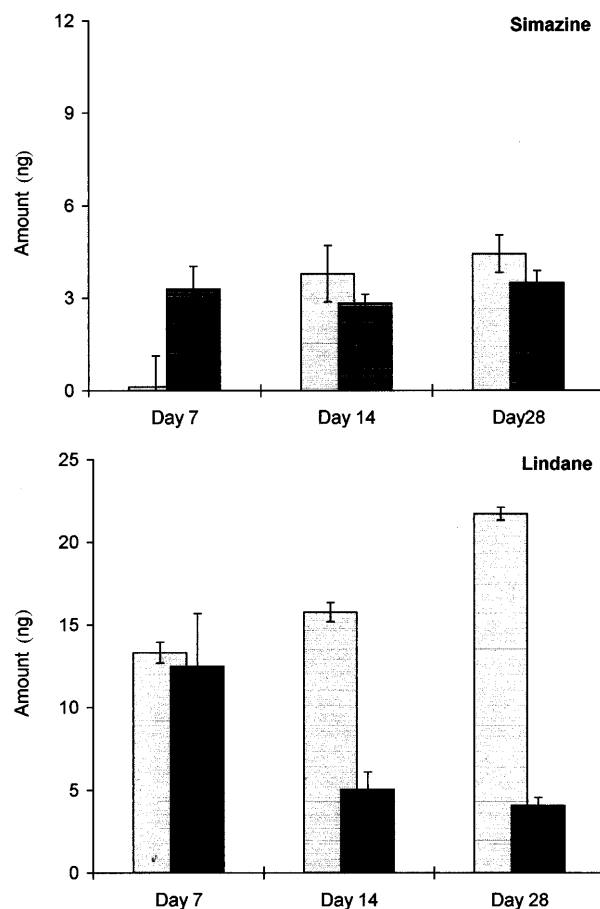


Fig. 5. Mass balance for Sediment II comparing (□) losses of the compounds from the overlying solution with (■) gains in the sediment; error bars show the standard deviation.

(11 mm) of Sediment I. After seven days, a concentration of $10 \mu\text{g kg}^{-1}$ simazine and lindane had penetrated ~ 30 mm. By the end of the experiment $10 \mu\text{g kg}^{-1}$ simazine had penetrated ~ 60 mm whereas $10 \mu\text{g kg}^{-1}$ lindane had penetrated to ~ 45 mm. In comparison, pesticide concentrations decreased with time in the top layer (11 mm) of Sediment II. After seven days, $10 \mu\text{g kg}^{-1}$ simazine and lindane had reached ~ 50 mm and by the end of the experiment, $10 \mu\text{g kg}^{-1}$ simazine had reached ~ 55 mm compared with $10 \mu\text{g kg}^{-1}$ lindane at ~ 35 mm. The concentration of pesticide in the top few millimetres increased with time for Sediment I and decreased for Sediment II. The difference in sorption affinities between the sediments could explain this; initially, the pesticides are quickly sorbed to Sediment II at higher concentrations because of the larger K_d .

The application of eqns (14) and (15) with the porosity and particle density values given in Table 1, the depth of the overlying solution (0.062 m), cross-sectional surface area (0.015 m^2) and the reduced Henry's Law constant from the K_d values in Table 2 is illustrated in Figs 6 and 7 where the calculated model sediment profiles can be compared with the observed results. Similarly, Fig. 3 shows the calculated change in pesticide concentration in the overlying solution com-

pared with that observed. Initial calculations showed that the optimisation for simazine was not very sensitive to the choice of K_d , so the distribution coefficients obtained in the sorption experiments were used. The optimised values of the effective diffusion coefficients (D') for sediments I and II are 5.1 and $8.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ respectively for simazine compared with 1.6 and $1.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ respectively for lindane. The minimum values of $Res(D')$ (eqn (16)) were 0.44 and 0.39 for simazine and 2.58 and 6.53 for lindane in Sediments I and II respectively. Reasonable agreement was obtained between the calculated and the observed results for simazine in Sediments I and II. Excellent agreement was obtained for lindane in Sediments I where the mass balance for the system was best. The agreement was worst for lindane in Sediment II at 28 days reflecting the poor mass balance (Fig. 5).

Using the effective diffusion coefficients (D') and reduced Henry's Law constant for each pesticide/sediment combination, eqn (9) was solved simultaneously using the data for the two sediments. The values of D_s and D_a calculated were 0.38 and $0.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ respectively for simazine compared with 6.16 and $0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for lindane respectively. No values for D_s and D_a in river sediments

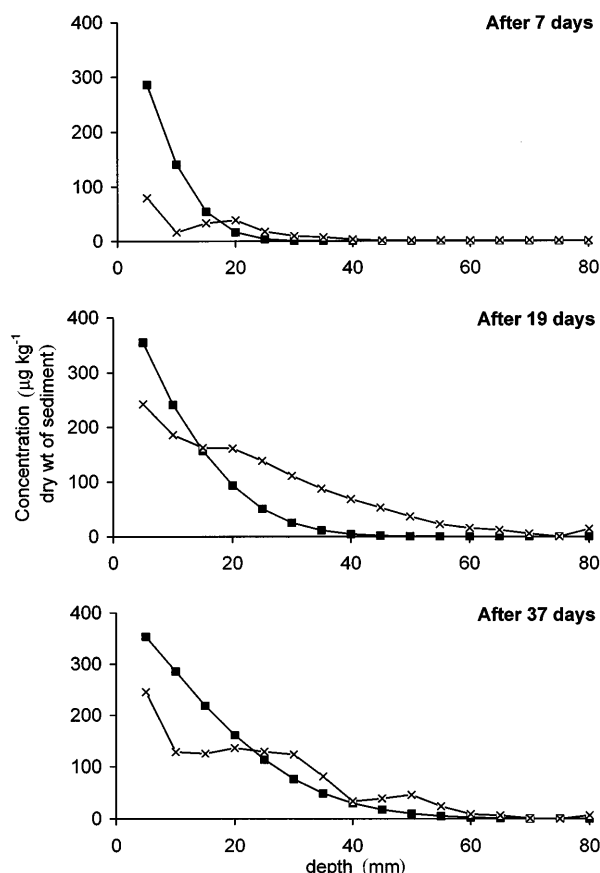


Fig. 6. Comparison of (... × ...) measured and (—■—) calculated concentrations of simazine in Sediment I at different times.

were found in the literature, but they are comparable with values of D_s and D_v for soils^{43,44} (where the effective diffusion coefficient is composed of diffusion in the dissolved phase, D_s , and diffusion in the vapour phase, D_v).

The effective diffusion coefficients, obtained *via* the model, are in good agreement with those found in the literature. The values for simazine are the same order of magnitude as found for another triazine, propazine, in a sandy soil.⁴⁵ However, the water contents in the propazine study were much lower, so diffusion in the dissolved and sorbed phases would have been constrained by the distribution of water in the sediment. The effective coefficients obtained for lindane in a silt loam soil⁴³ were two orders of magnitude smaller than those obtained in this study. The silt loam also had lower water contents than the sediment in this study, so diffusion in the dissolved phase was again constrained. The difference in the sorption coefficients between the silt loam and the river sediment in this study could have produced the lower effective diffusion coefficients, particularly for lindane where sorbed molecules are effectively immobile (compared with simazine where diffusion in the dissolved and sorbed phases was found to be similar).

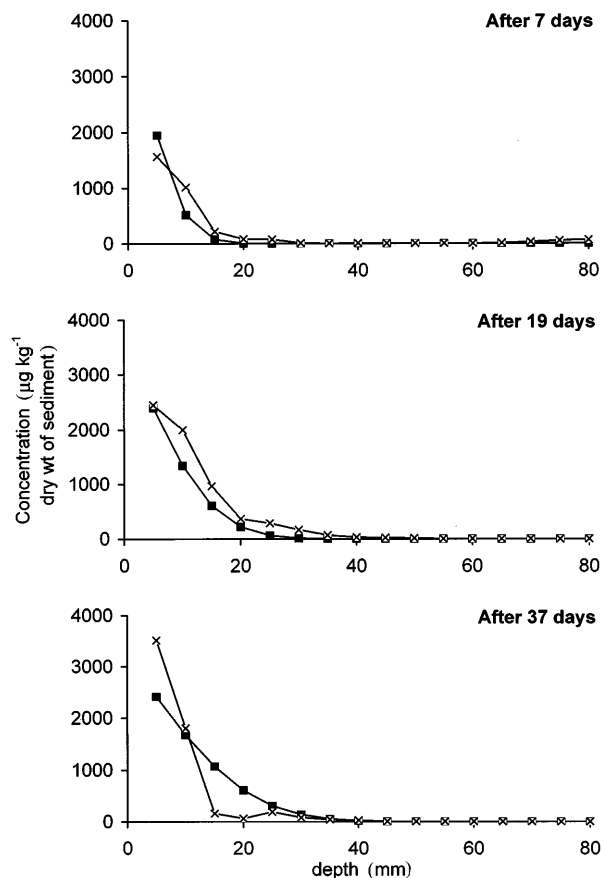


Fig. 7. Comparison of (... × ...) and (—■—) calculated concentrations of lindane in Sediment I at different times.

The Wilke–Chang and Stokes–Einstein equations,⁴⁶ describing the diffusion of molecules in a solvent, were used to calculate the diffusivities of simazine and lindane in water at 10°C. The Wilke–Chang equation produced a diffusion coefficient of $5.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for simazine and the Stokes–Einstein gave $4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for lindane. The latter is in reasonable agreement with the value of $6.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ found in this study for lindane but the predicted value for simazine in the bulk water is much larger than the value for porewater computed using the model, *viz* $0.38 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This implies that the porewater environment for simazine is very different from the bulk water and, because D_s and D_a are of similar magnitude, is expected to be closer to that experienced in the sorbed state. This must reflect the more polar nature of simazine compared with lindane and how the molecule interacts with ions and surfaces in the sediment.

On first appearances, the results in Figs 1 and 2 suggests that simazine should have a greater effective diffusion coefficient than lindane, because it travels down the sediment profile faster. However, lindane is much less mobile than simazine in the sorbed state, as reflected in its smaller value for D_a . Thus, even though lindane has a greater value of D_s than simazine, sorption to particulate matter impedes its movement. Diffusion of simazine

in the porewater and sorbed layer is similar which is consistent with the more polar nature of the molecule compared with lindane.

5 CONCLUSIONS

Profiles of simazine and lindane in tests with river-bed sediment showed pesticide penetration from an overlying aqueous solution into clean sediment to a maximum depth of 89 mm over a 37-day period. Concentrations decreased with depth and the compounds' penetration increased with time. The observed results compared well with the calculated results, especially where there was a good mass balance between amounts of pesticide in the sediment and that lost from the overlying solution. Effective diffusion coefficients calculated for each pesticide/sediment system were used to obtain values for pesticide diffusion in the porewater and sorbed phases. Diffusion in the porewater was 0.38×10^{-10} and $6.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for simazine and lindane respectively and diffusion in the sorbed phase was $0.39 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for simazine and negligible for lindane.

Transport by diffusion, taking into account sorption interactions, was used to explain the observed concentration profiles. It was found that sorption significantly influenced the rate of diffusion of the compounds. Lindane had a larger effective diffusion coefficient than simazine but its overall rate of penetration into the sediment was retarded because of its larger sorption and negligible diffusion in the sorbed phase.

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